Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems

Quarterly Technical Progress Report

July 1, 2005 – September 30, 2005

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ABSTRACT

This document summarizes progress on Cooperative Agreement DE-FC26-04NT41992, “Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems,” during the time-period July 1, 2005 through September 30, 2005. The objective of this project is to demonstrate at pilot scale the use of solid honeycomb catalysts to promote the oxidation of elemental mercury in the flue gas from coal combustion, and the use of a wet flue gas desulfurization (FGD) system downstream to remove the oxidized mercury at high efficiency. The project is being co-funded by the U.S. DOE National Energy Technology Laboratory, EPRI, Great River Energy (GRE), TXU Generation Company LP, the Southern Company, and Duke Energy. URS Group is the prime contractor.

The mercury control process under development uses honeycomb catalysts to promote the oxidation of elemental mercury in the flue gas from coal-fired power plants that have wet lime or limestone FGD systems. Oxidized mercury is removed in the wet FGD absorbers and leaves with the byproducts from the FGD system. The current project is testing previously identified catalyst materials at pilot scale and in a commercial form, to provide engineering data for future full-scale designs. The pilot-scale tests will continue for approximately 14 months or longer at each of two sites to provide longer-term catalyst life data.

Pilot-scale wet FGD tests are being conducted periodically at each site to confirm the ability to scrub the catalytically oxidized mercury at high efficiency. The pilot wet FGD system has also been used downstream of catalysts being tested as part of another cooperative agreement (DE-FC26-01NT41185).

This is the seventh reporting period for the subject Cooperative Agreement. During this period, project efforts primarily consisted of operating the catalyst pilot unit at the TXU Generation Company LP’s Monticello Steam Electric Station, including routine catalyst activity measurement efforts. Also during the quarter, minor refurbishment was completed on the second pilot unit, and it was shipped to Georgia Power’s Plant Yates for installation there. This Technical Progress Report presents catalyst activity results from the oxidation catalyst pilot unit at Monticello and discusses the status of the second pilot unit.

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INTRODUCTION

This document is the quarterly Technical Progress Report for the project "Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems," for the time-period July 1 through September 30, 2005. The objective of this project is to demonstrate at pilot scale the use of solid honeycomb catalysts to promote the oxidation of elemental mercury in the flue gas from coal combustion, and the use of a wet flue gas desulfurization (FGD) system downstream to remove the oxidized mercury at high efficiency. The project is being co-funded by the U.S. DOE National Energy Technology Laboratory, EPRI, Great River Energy (GRE), TXU Generation Company LP (TXU Generation), Southern Company, and Duke Energy. URS Group is the prime contractor.

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Four utility team members are providing project host sites for mercury oxidation catalyst testing. GRE provided a test site at their Coal Creek Station (CCS), which fires North Dakota lignite, and City Public Service of San Antonio (CPS) is providing a test site at their J.K. Spruce Plant, which fires Powder River Basin (PRB) subbituminous coal. Both the CCS and Spruce mercury oxidation catalyst pilot tests have been conducted as part of project 41185. Both have hosted pilot FGD tests downstream of the catalysts as part of the current, 41992 project.

In the current project, TXU Generation is hosting pilot catalyst tests and intermittent wet FGD pilot tests at their Monticello Steam Electric Station, Unit 3, which fires a Texas lignite/Power River Basin (PRB) coal blend. The TXU Generation test program began in mid-January 2005.

Duke Energy was also to host oxidation catalyst pilot and wet FGD pilot tests at one of their sites firing low-sulfur Eastern bituminous coal. However, both of their candidate sites (that are having wet FGD retrofitted but not selective catalytic reduction) were measured to have low elemental mercury concentrations in the flue gas downstream of the particulate control device. Consequently, Duke Energy decided not to host oxidation catalyst pilot tests. However, they did host pilot wet FGD tests to determine the ability to scrub the highly oxidized mercury content of the particulate control outlet flue gas at their Marshall Station.

Southern Company has a number of generating units that fire low-sulfur Eastern bituminous coal. They have agreed to host oxidation catalyst tests at their Georgia Power Plant Yates, Unit

1, and to provide project co-funding. Oxidation catalyst pilot tests will commence there during the fourth quarter of calendar year 2005.

The remainder of this report presents results from this project for the third quarter of calendar year 2005. The report is divided into five sections: an Executive Summary followed by a section that describes Experimental procedures, then sections for Results and Discussion, Conclusions, and References.

EXECUTIVE SUMMARY

Summary of Progress

The current reporting period, July 1 through September 30, 2005, is the seventh technical progress report period for the project. During the current period, the oxidation catalyst pilot unit continued in operation at Monticello Unit 3. One catalyst activity measurement trip was made to Monticello in mid-July. Also during the quarter, refurbishment of the second pilot unit was completed, and it was shipped from URS's Austin office to Georgia Power's Plant Yates so that it can be installed there.

Problems Encountered

There were no significant problems encountered during the current reporting period other than technical issues that are discussed later in this report.

Plans for Next Reporting Period

During the next reporting period (October 1 through December 31, 2005), catalysts will be evaluated for elemental mercury oxidation activity at Monticello through routine (~bimonthly) evaluation trips. The second oxidation catalyst pilot unit will be started up at Plant Yates.

Prospects for Future Progress

During the subsequent reporting period (January 1 through March 31, 2006), catalysts will be evaluated for elemental mercury oxidation activity at Monticello through routine (~bimonthly) evaluation trips. The oxidation catalyst pilot unit at Plant Yates should be in operation and also be evaluated for elemental mercury oxidation activity through routine evaluation trips. Intensive gas characterization efforts and initial wet FGD pilot testing will likely occur at Plant Yates during the quarter.

EXPERIMENTAL

The work being conducted as part of this project will use three different experimental apparatus types. One is an elemental mercury catalyst oxidation pilot unit (8000 acfm of flue gas treated), the first of which was recently installed at TXU Generation's Monticello Steam Electric Station. A second, nearly identical pilot unit was previously located at CPS' Spruce Plant. During the course of this project, this second pilot unit has been relocated and installed at Georgia Power's Plant Yates.

Each pilot unit has four separate compartments that allow four different catalysts to treat flue gas from downstream of the host plant's particulate control device. Details of the pilot unit design, construction, catalyst preparation and pilot unit operation have been discussed in previous quarterly technical progress reports as part of the 41185 project[1, 2, 3, 4].

The second pilot unit, which has now been shipped to Plant Yates, did not have sonic horns installed on it while it was in operation at CPS' Spruce Plant. Spruce has a fabric filter for particulate control and sonic horns did not prove to be needed to keep the catalyst clean there. In anticipation of operating downstream of a small-SCA ESP at Plant Yates, new sonic horns were installed prior to shipping the pilot unit. The first pilot unit at Monticello has 17-inch horns that were supplied by Analytec Corporation. Since those horns were procured, Analytec was purchased by BHA, who markets a similar horn of their own design. Consequently, the second pilot unit had BHA rather than Analytec horns installed.

The activity of the catalysts is determined by measuring the change in elemental mercury concentration across each catalyst, while ensuring that the total mercury concentrations do not change significantly across the catalyst. These measurements are primarily conducted using a mercury semi-continuous emissions monitor (SCEM) developed with funding from EPRI. The analyzer has been described in a previous report[5]. Periodically, the analyzer results are verified by conducting manual flue gas sampling efforts in parallel across each catalyst chamber by the Ontario Hydro method.

The flue gas sampling system for the second pilot unit was modified prior to shipping to Plant Yates to allow the possibility of using two SCEMs to simultaneously sample catalyst inlet and outlet flue gas. Originally, both pilot units were equipped with a sampling manifold and solenoid valves that selected flue gas from the catalyst inlet or the outlet of any of the four catalyst chambers. On analyzer could be cycled to analyze flue gas from any of these five locations. The selected flue gas sample was then drawn through an inertial gas separator (IGS) filter by a centrifugal blower, and the gas sample to the SCEM was withdrawn radially from the IGS filter. With the modification to the second pilot unit, it now has two IGS filters and two blowers, one dedicated to pilot unit inlet flue gas and the second connected via manifold and solenoid valves to the outlets of the four catalyst chambers. This allows the use of two analyzers to simultaneously analyze catalyst inlet and outlet flue gas. If only one analyzer is used, its inlet tubing will have to be physically moved from the inlet to the outlet sampling loops to quantify catalyst performance.

The second experimental apparatus used as part of this project is a bench-scale test unit that is used to evaluate the activity of candidate catalyst samples under simulated flue gas conditions. The bench-scale catalyst oxidation test apparatus was previously described in quarterly technical progress reports for the 41185 project[3, 4].

The third experimental apparatus is a pilot-scale wet FGD unit that was designed and fabricated as part of the current, 41992 project, to allow the measurement of how effectively catalytically oxidized mercury can be scrubbed. The pilot unit was designed to treat the flue gas from one of four catalyst chambers on either of the mercury oxidation catalyst pilot units. The design basis and a simplified piping and instrumentation diagram (P&ID) for the pilot wet FGD system were included in a previous technical progress report for this project.[6]

RESULTS AND DISCUSSION

This section provides details of technical results available from the current reporting period, July 1 through September 30, 2005. Pressure drop and activity results are presented for the catalysts installed in the catalyst pilot unit at Monticello. No results are available yet from the pilot unit that was moved from Spruce Plant to Plant Yates during the quarter.

Catalyst Pilot Unit Operation at Monticello

The catalyst pilot unit was started up in flue gas service at Monticello Steam Electric Station, near Mount Pleasant, Texas, on January 14, 2005, and has operated continuously since then other than during short, unscheduled host unit outages. The physical characteristics of the four catalysts currently installed are summarized in Table 1.

Table 1. Characteristics of Catalysts Installed in Pilot Unit at Monticello

Catalyst Box Number	Catalyst	Cross Section, in x in (m x m)	Catalyst Depth	Cell Pitch, mm	Cells per Sq. In. (CPSI)	Area Velocity, std. ft/hr
1	Pd #1 (Johnson Matthey)	29.5 x 29.5 (0.75 x 0.75)	9 in. (0.23 m)	3.2	64	52
2	SCR (Cormetech/MHI)	35.4 x 36.2 (0.90 x 0.92)	29.5 in. (0.75 m)	3.3	58	11
3	Gold (Sud-Chemie Prototech)	29.5 x 29.5 (0.75 x 0.75)	3 x 3 in. (3 x 0.08 m)	3.2	64	52
4	Pd #1 (regenerated from CCS)	29.5 x 29.5 (0.75 x 0.75)	3 x 3 in. (3 x 0.08 m)	3.2	64	52

Catalyst Pressure Drop Performance

In previous catalyst testing at CCS, fly ash was observed to build up in the horizontal-gas-flow catalyst cells, resulting in increased catalyst pressure drop and lowered catalyst oxidation performance. Sonic horns were installed and were generally effective in preventing fly ash buildup. Since Monticello, like CCS, has an ESP for particulate control (Spruce has a reverse-gas fabric filter), it was expected that the sonic horns would be necessary to prevent fly ash buildup there.

The sonic horns were placed in service on the catalyst pilot unit at the end of January, two weeks after initial pilot unit startup on January 14, 2005. However, the sonic horns did not operate properly through the remainder of that quarter. During that period, a failed compressed air pipe nipple was replaced, the horn timer was replaced, the solenoid valves controlling air flow to the horns were replaced, the horns were disassembled and cleaned, and an air pressure regulator was installed to ensure that the optimum air pressure of 70 psig was supplied to the horns. While these efforts corrected a number of operational issues, it still remained that the solenoid valves controlling air flow to the horns did not turn off properly at the end of their cycle (the horns are intended to sound 10 seconds each every half hour).

In April, one solenoid valve that had been particularly problematic was replaced with a larger valve (3/4-inch vs. ¼-inch). This change, along with minor wiring and tubing changes, resulted in all four valves cycling properly beginning in late April. The four horns appear to have cycled properly through approximately mid-June.

The pressure drop across all four catalysts saw a large increase starting in mid-June, again apparently caused by sonic horn malfunction. Although the air line to the sonic horns has a regulator and filter to control the air pressure and to remove impurities from the compressed air, the air line upstream of the regulator is rusty on the inside. During continued horn operation, exfoliated rust particles from the line tend to build up in the regulator inlet, eventually plugging air flow to the regulator. The regulator was found plugged and was cleaned twice during the current quarter. During the upcoming quarter, a basket strainer will be installed on the air line upstream of the regulator in an effort to prevent future plugging.

Figure 1 shows the “full load” pressure drop data for all four catalysts from start up through early October 2005. “Full load” was defined as periods where the flue gas flow rate through the highest-flowing catalyst (gold) was at least 1900 acfm. The desired flow rate is 2000 acfm for all four catalysts.

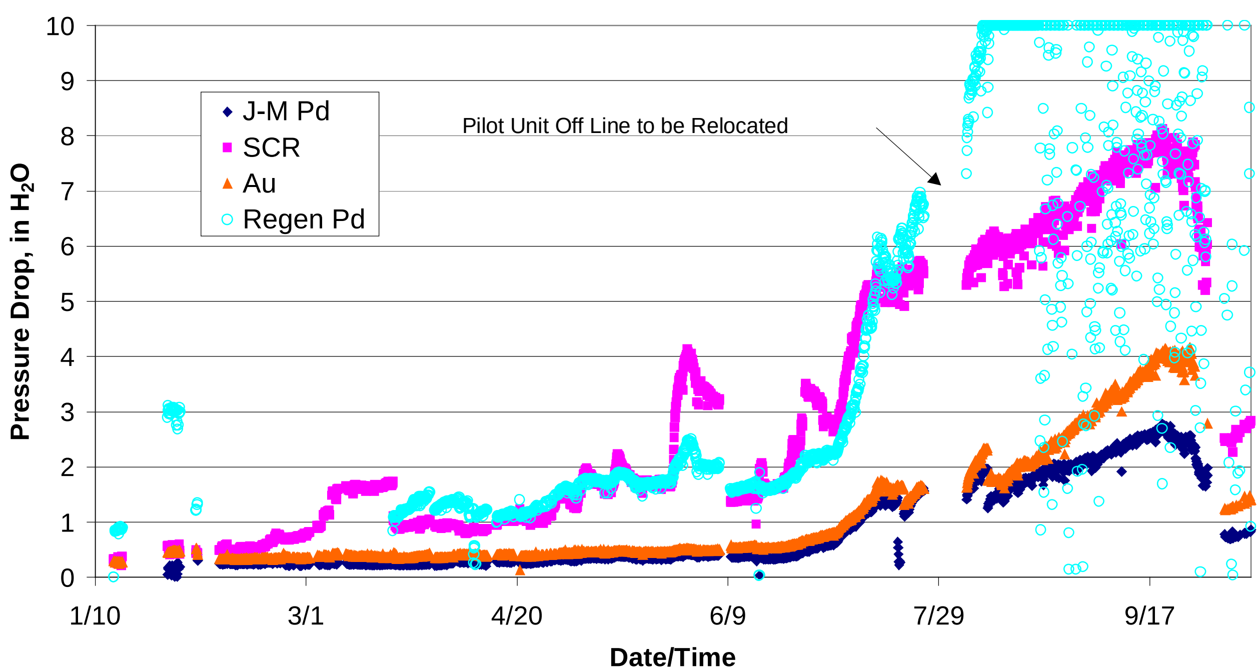

Figure 1. Full-load Catalyst Pressure Drop Data from Monticello Pilot Unit

As noted on the figure, there was a period of about one week where the pilot unit was off line to be moved. The move was required because of construction activity in the vicinity of the pilot unit. This move exacerbated the pressure drop buildup across the catalysts, because after the move, the pilot unit was placed back in service but the air to the sonic horns was not turned back on. The pilot unit operated about five days with no air to the sonic horns before this oversight was discovered and corrected.

The data in Figure 1 show that the pressure drop across all four catalysts increased markedly during periods the sonic horns were not operating properly. The pressure drop across the Johnson-Matthey Pd increased to approximately 2.5 in. H_2O, and the drop across the gold catalyst increased to about 4 in. H_2O. The pressure drop across the SCR catalyst increased to as high as 8 in. H_2O, while the pressure drop across the regenerated Pd catalysts exceeded 10 in. H_2O. These pressure drop increases, related to fly ash buildup in the catalyst flow channels, no doubt contributed to the apparent loss in catalyst activity measured during the quarter, as discussed below.

Late in the quarter, the air pressure regulator inlet was cleaned of rust particles and sonic horn operation was restored. The pressure drop across all four catalysts began to drop. At the end of September, Unit 3 had a short outage, during which the sonic horns continued to operate. Apparently this horn operation during low air flow through the pilot unit helped remove fly ash from the catalyst flow chambers. Immediately after the outage, the pressure drop across all four catalysts was greatly reduced – down to less than 1 in. H_2O for the Johnson-Matthey Pd.

In spite of the improvement in pressure drop noted, it was decided to shut down and physically clean fly ash from the catalysts. This cleanup was conducted during the second week of October. Plugged, or partially plugged pressure drop tubing connections were found at the inlets to several of the catalyst boxes, which may have contributed to erroneous pressure drop readings. Catalyst activity measurements for the cleaned catalysts will be made later in October.

Elemental Mercury Oxidation Activity Performance

The activity of these four catalysts for oxidizing elemental mercury was measured once during the quarter, in mid July. The results of these measurements are shown in Table 2. Most of the total mercury concentration data were measured on the first day, and elemental mercury concentrations were measured the second. Thus, mercury breakthrough/adsorption data across the catalysts are typically available only for the first measurement day, while mercury oxidation data across the catalysts are typically only available for the second measurement day.

The results in Table 2 show a significant decline in mercury oxidation activity across all four of the catalysts since the previous measurements. This decline is also illustrated in Figure 2. The figure is illustrated to show linear trends for activity loss versus time for each of the four catalyst types, extrapolated through the end of the quarter. However, there is quite a bit of scatter in the data, particularly for the SCR and Johnson Matthey Pd. The data show that these two catalysts are also the least active, at 26% or less oxidation of elemental mercury. However, it is known that as of mid-July a considerable amount of fly ash had built up in these catalysts due to the sonic horn operation issues described above. Measurements are planned for October, after the catalysts are physically cleaned, to determine how much of the apparent activity loss for these catalysts is due simply to fly ash buildup in the catalyst flow channels.

Table 2. Results of Catalyst Activity Measurements at Monticello, July 2005 (all values represent daily averages)

Sample Location (Sampling Date)	Hg Concentration, mg/Nm^3 @ 3% O_2*				Total Hg % Oxidation		% Hg Adsorption Across Catalyst	% Hg Oxidation Across Catalyst
	Catalyst Inlet		Catalyst Outlet					
	Total Hg	Elemental Hg	Total Hg	Elemental Hg	Catalyst Inlet	Catalyst Outlet		
SCR (7/19)	31.1	-	28.5	-	-	-	8	-
SCR (7/20)	-	5.23	-	5.49	-	-	-	-5
J-M Pd #1 (7/19)	30.9	12.4	29.1	9.24	60	68	6	26
J-M Pd #1 (7/20)	-	5.26	-	5.27	-	-	-	0
Regenerated Pd #1 (7/19)	29.9	-	25.9	-	-	-	13	-
Regenerated Pd #1 (7/20)	-	7.05	-	3.80	-	-	-	46
Gold (7/19)	34.9	-	31.4	-	-	-	10	-
Gold (7/20)	11.0	4.03	-	1.19	63	89	-	70

*1 µg/Nm^3 @ 3% O_2 = 0.67 lb Hg/10^{12} Btu heat input

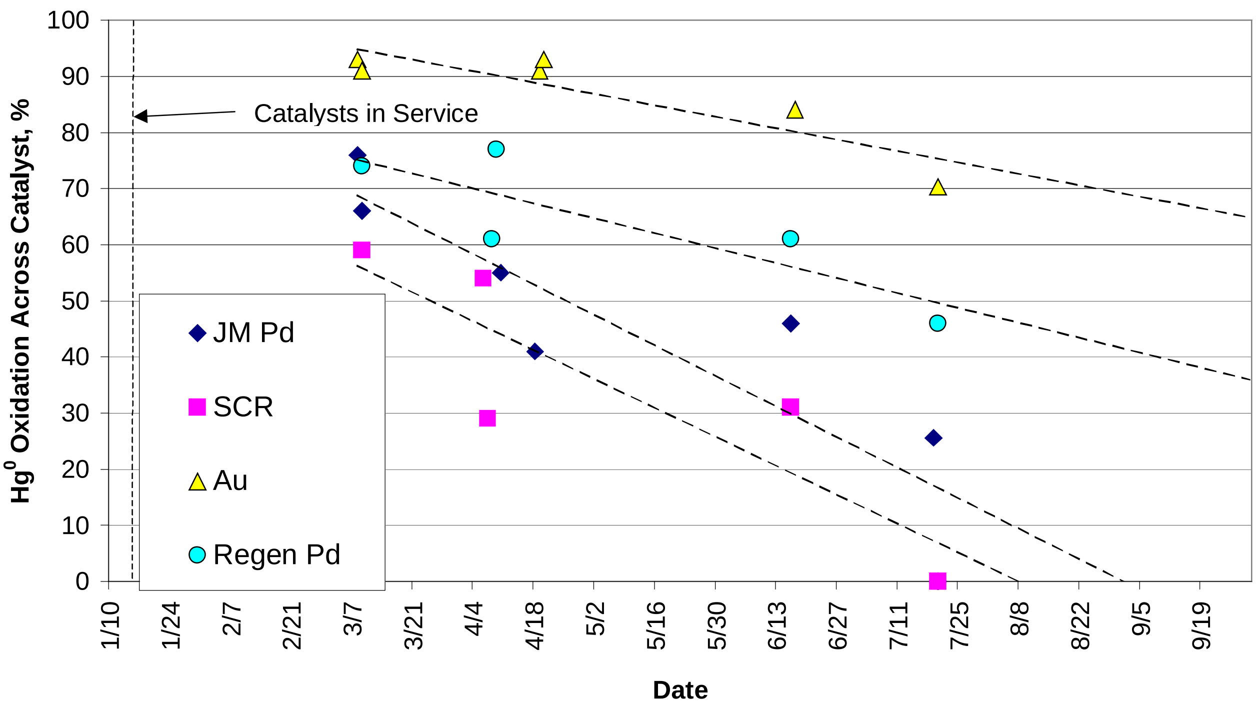

Figure 2. Elemental Mercury Oxidation Activity versus Time for Catalysts at Monticello

Also, as discussed in the previous Quarterly Technical Progress Report, there is evidence that the Hg SCEM used to quantify catalyst oxidation performance tends to under-report the performance of the SCR and Johnson-Matthey Pd catalysts compared to Ontario Hydro method results.[7] This may also contribute to the lower activity measured for those two catalyst types. Future Ontario Hydro relative accuracy measurements will confirm the activity of these catalyst types.

CONCLUSION

Results to date show that reliable sonic horn operation will be required to prevent fly ash buildup in the horizontal-gas-flow catalysts, particularly the SCR catalyst and the regenerated palladium catalyst.

Catalyst activity test results show that gold is the most active of the four catalysts being tested at Monticello Station. Measurements by mercury SCEM in July show that the activity of the gold catalyst had decreased to 70%. The SCEM results rank the regenerated palladium, Johnson Matthey palladium, and the SCR catalysts in decreasing order of mercury oxidation activity.

However, it is likely that the activity of all four catalysts has been adversely affected by fly ash buildup in the catalyst chambers. Measurements in October, after the catalysts have been physically cleaned of fly ash buildup, should indicate how much of the apparent loss was due to fly ash effects. Also, these apparent losses have not been confirmed by Ontario Hydro method measurements. The next planned Ontario Hydro method measurements at this site are to be conducted in the fourth quarter of this calendar year.

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